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Kinetic Models in Heterogeneous Catalysis

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The role and importance of chemical kinetics in heterogeneous catalysis at the present stage of development are examined and the concept of kinetic models, in the exact, reliable, complete, and well-founded form, as well as the usefulness of combined kinetic investigations for the determination of these models are discussed. The effectiveness of combining different methods for devising informative models of this kind, examples of which are quoted, is demonstrated. The problems involved in setting up non-steady-state kinetic models, which are some of the most important in chemical kinetics, are briefly described. The optimum characteristics of kinetic models and the relation between the properties of the latter and the characteristics of reaction selectivities are analysed. The kinetic aspects of tests of the activities and selectivities of catalysts of complex reactions are mentioned in conclusion.
The bibliography includes 202 references.

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I. INTRODUCTION

The principal trend in theoretical research into heterogeneous catalysis is the determination of a relation between the properties of the surface layer of catalysts and the characteristics of the processes which they accelerate. Progress in this direction requires a profound understanding of the time course of catalytic processes, which determines the status of chemical kinetics in heterogeneous catalysis and gives rise to the idea of its "kinetic foundation".

Although the creation of such foundation was begun by the early investigations of Langmuir, Hinshelwood, and Schwab, the role and importance of the kinetics of heterogeneous catalytic reactions became evident only comparatively recently, this being promoted by the factors listed below:

(1) The spread of accurate kinetic experimental techniques[1-3], which make it possible to obtain reliable data without the distorting influence of factors which were previously not taken into account.

(2) The development of a theory of complex reactions[4-6] whereby one can approach an understanding of the kinetics without undue simplifications.

(3) The extension of the theory of macrokinetics to permit the estimation of transport parameters in the course of reactions and the inclusion of real process conditions [7,8].

(4) The employment of computer techniques and the increase in the scope of the mathematical analysis of kinetics and kinetic problems [9-11]. The operation of these factors clearly established the role of chemical kinetics as a science and the possibility of its theoretical employment to establish one of the necessary procedures for the elucidation of the mechanisms of catalytic reactions as well as its practical employment in one of the stages of the incorporation of the technology of catalytic processes in industry and its improvement. Table 1 gives a brief compilation of processes for which reactors have been simulated in recent years and the optimum conditions analysed on the basis of kinetic data [12-40]. In Boudart's review [41], a greater importance is already attributed to the practical aspects of the employment of kinetics than to its theoretical aspects. However, both aspects of the problem are so closely interrelated and inseparable that preference should not be given to either.

Table 1. Examples of processes for which modelling and optimisation have been carried out using kinetic data.

Process and catalyst	Result	Refs.
Selective hydrogenation of phenol; Pd	Calculation of optimum conditions for the operation of reactor	12
Selective hydrogenation of ethynyldimethylmethanol; Pd	Reactor model	13
Liquid-phase hydrogenation of heptene; Ni	Analysis of reactor model	14
Conversion of glucose into glycerol; Ni	Optimum reactor design	15
Reduction of nitrobenzene; Cu	Calculation and selection of reactor dimensions	16
Hydrogenation of dichloronitrobenzene to dichloroaniline; Pt	Reactor design	17
Hydrogenation of fats on different catalysts	Design of large-scale apparatus	18
Dehydrogenation of butane and butene; Al-Cr	Optimum conditions	19
Dehydrogenation of isopentenes to isoprene; Ca-Ni-P	Optimum conditions	20
Dehydrogenation of ethanol; Cu	Optimum conditions	21
Oxidative dehydrogenation of butenes; Zn-Cr-Fe	Modelling of an adiabatic reactor	22
Oxidation of propene; Co-Mo	Optimum diameter of a tubular reactor and process parameters	23
Oxidation of benzene to maleic anhydride; V_2O_5	Calculation of reactor model parameters	24
Oxidation of *o*-xylene; V_2O_5	Reactor model and optimum conditions	25,26
Oxidation of naphthalene in a fluidised bed; V_2O_5	Reactor model	27
Oxidation of methanol; Ag	Reactor model and optimum conditions	28
Oxidation of anthracene; V_2O_5	Calculations on reactor operation	29
Oxidative chlorination of ethylene in a fluidised bed; $CuCl_2$	Calculations of the parameters and optimum conditions	30
Extensive oxidation of pentane; Al-Pt	Reactor model and optimum conditions	31
Extensive oxidation of phenol; Al-Pt	Optimum reactor design, analysis of stability	32
Extensive oxidation of methyl methacrylate; Al-Pt	Reactor conditions, analysis of stability	33
Oxidation of HCl in a fluidised bed of chlorides, Cu, Sn, and K	Analysis of reactor operation	34
Oxidation of sulphur dioxide; V_2O_5	Optimum reactor model	35
Conversion of CO by water vapour, Fe-Cr and Cr-Sn	Optimum parameters of the reactor for a two-stage process	36
Conversion of methane by water vapour; Ni	Optimum parameters of a tubular reactor	37
Hydrochlorination of acetylene on Hg_2Cl_2	Process optimisation and calculation of reactor parameters	38
Dehydration of α-hydroxyisobutyric acid on calcium phosphate	Calculation of reactor parameters	39
Demethylation of toluene by water vapour; Rh-Al	Calculation of the parameters of a cascade of reactors	40

The central task of kinetics in heterogeneous catalysis at the present stage is the creation of kinetic models of various catalytic processes and a comparison and generalisation of these models. This task is particularly urgent in the light of the fact that further development of catalysis at the present time can apparently involve primarily the elucidation and accumulation of special and general relations rather than the creation of new universal theories.

On the basis of the foregoing, we shall consider the problem of kinetic models in heterogeneous catalysis and the extent to which it can be described by these models. Ways for the effective creation of kinetic models and certain problems associated with the properties of the models and the characteristics of catalytic processes will be discussed.

II. CHARACTERISTICS OF KINETIC MODELS

A quantitative characteristic of a process in the form of a mathematical description of its velocities (in the presence of a given catalyst) in the different directions realised under specified conditions, based on multistage mechanisms reflecting the general characteristics of the reaction, and carrying the necessary information about the catalyst and about significant non-steady-state changes as a function of different factors, will be regarded as a kinetic model. Multistage mechanisms (proved or hypothetical) indicate the sequence and stoichiometry of the transformations of the intermediate compounds. The availability of data for the ratios of the rates of the stages under the conditions investigated permit simplifications in the complete mathematical description of the rate of the process. In considering a kinetic model, we can speak of its form, implying by this a mathematical description of the rate of the process and the factors influencing it (including factors causing a change in the activity of the catalyst) and of the content of the model, i.e. the characteristic features which give rise to the given form.

Such traetment of the concept of the kinetic model differs significantly from the concept of reaction mechanism—the comprehensive qualitative characteristic of its internal features in the presence of the given catalyst under the specified conditions, reflecting the nature of the intermediate species produced at the elementary stages as well as their coupling. In the kinetic model, the principal factor is tested and detailed information about the changes in the rate of the process, while in the concept of reaction mechanism the main factor is detailed information about the nature, properties, and interconversions of the intermediates. The simplest step in the change of the chemical state of the system, involving the overcoming of not more than one energy barrier corresponding to the formation and decomposition of a single activated complex, must be regarded as an elementary stage.

In its broad sense, the kinetic model serves as a most important process characteristic, which may be tabulated for a given catalyst under specified conditions. The model must therefore be exact, reliable, complete, and well-founded. The accuracy of the kinetic model is determined primarily by the accuracy of the experimental methods used to establish it. Gradient-free methods [1-3], which make it possible to obtain accurate kinetic data under steady-state conditions, are nowadays generally accepted for this purpose. They can be supplemented by non-steady-state methods for the elucidation of the influence of the reaction system on the catalyst, the characteristics of its activation, and the changes in the activity and behaviour of the catalyst under non-steady-state conditions [42,43]. The reliability of the model depends not only on the experiment but also on its treatment and interpretation, taking into account all the factors influencing the kinetics, and

Table 2. The ambiguity of certain kinetic equations and process mechanisms.

Reaction	Kinetic equation	Multistage mechanism	Remarks
Hydrochlorination of acetylene on $HgCl_2$ (Ref.53)	$r = k\frac{P_{C_2H_2}P_{HCl}}{1 + k'P_{C_2H_2} + k''P_{HCl}}$ $r = k\frac{1 + k'(1 + k''P_{HCl})P_{C_2H_2}P_{HCl}}{(1 + k_1P_{HCl})(1 + \frac{k_2P_{C_2H_2}}{1 + k_3P_{HCl}} + k_4P_{HCl})}$	—	Both equations describe kinetic data equally well
Hydrogenation reaction $A + H_2 = AH_2$ (Ref.54)	$r = kP_A^{1-m}P_{H_2}$	I. 1) $A = A_{ads}$; 2) $A_{ads} + H_2 = AH_2$(slow) II. 1) $H_2 = 2H_{ads}$; 2) $2H_{ads} + A = AH_2$(slow) III. 1) $A + H_2 + [K] = A[K]\cdot H_2$ (slow) 2) $A[K]\cdot H_2 = AH_2 + [K]$	All three mechanisms lead to the same kinetic equation
Conversion of methane by water vapour (Ref.55)	$r = k\frac{P_{CH_4}P_{H_2O}\gamma}{P_{H_2O} + k_1P_{H_2} + k_2P_{H_2}^2 + k_3P_{H_2}^3}$ (γ = correction for effect of reverse reaction)	"Oxidative mechanism" 1) $CH_4 = CH_{2ads} + H_2$ 2) $CH_{2ads} + H_2O = CHOH_{ads} + H_2$ 3) $CHOH_{ads} = CO_{ads} + H_2$ 4) $CO_{ads} = CO$ "Dehydrogenation mechanism" 1) $CH_4 = CH_{2ads} + H_2$ 2) $CH_{2ads} = C_{ads} + H_2$ 3) $C_{ads} + H_2O = CO_{ads} + H_2$ 4) $CO_{ads} = CO$	The same kinetic equation corresponds to both mechanisms

on the choice of the most adequate and unambiguous mathematical description of the process. Numerous methods involving the use of computers and experimental design have been developed for this purpose [10,11,44-51]. The completeness of the model depends on the width of the range of variation of the process conditions under which it is investigated and on the allowance for all possible pathways contributing to the observed features. Secondary pathways are frequently significant under these conditions (even when their contribution to the overall rate of the process is slight; see, for example, Spivak et al.[52]); also important is allowance for non-steady-state transitions (including those due to changes in the catalyst activity), the influence of the reaction mixture on the composition of the surface layer, the blocking of the surface by coke or other substances, etc. Depending on the purpose of the models, their completeness may be various. Finally, in order to prove the validity of kinetic models it is desirable that other physicochemical methods as well as kinetic methods should be used in devising them. This is because the application of kinetic experimental techniques and kinetic computational procedures alone can frequently lead to ambiguous models, examples of which are illustrated in Table 2. The examples[53-55] show that kinetic data, even those obtained by exact methods over a wide range of variation of conditions, can be described equally well by different fairly complex equations. On the other hand, various mechanisms and hence various multistage schemes can correspond to the same simple or complex kinetic equation.

Although numerous new physical methods, which can be used successfully (although still insufficiently) in catalysis for the elucidation of the nature of the intermediate species (see, for example, McCarroll[56]) have become available in recent years, the results obtained with their aid but without kinetic justification can also prove to be ambiguous. An example is provided by the decomposition of formic acid. The conclusion had been reached previously on the basis of infrared spectroscopic and adsorption studies[57,58] that the dehydrogenation of formic acid in the presence of nickel proceeds via the formation and slow decomposition of a surface formate. In a later study[59] it was shown (by combining the same measurements with kinetic data) that the rate of reaction decreases with increasing concentration of the surface formate. This introduces significant corrections to the earlier mechanism (the reaction proceeds on the part of the surface which is not blocked by the formate, apparently via the formation and decomposition of carboxylate complexes).

Conclusions reached solely on the basis of kinetic studies, even as regards the slow stage of the process, can be equally unreliable. Thus a study of the kinetics of the hydrogenation of cyclohexene in the presence of nickel and calculations of the absolute reaction rate led to the conclusion[60] that the process proceeds via a slow surface interaction of the two components. However, the present author's investigations[61,62] (where isotope exchange in cyclohexene and cyclohexane was studied in addition to reaction kinetics, measurements were made of the kinetic isotope effects, and the rates of the individual stages were compared using the ^{14}C label) showed that the process proceeds via the slow formation of a surface compound of cyclohexene followed by its rapid interaction with hydrogen†.

Thus in the general case, the kinetic model must not be justified by kinetic data alone, while, on the other hand, the corresponding reaction mechanism and the corresponding multistage schemes cannot be reliably established solely by means of the pyhsicochemical methods designed for this purpose without combining them with kinetic measurements. Hence the kinetic foundation

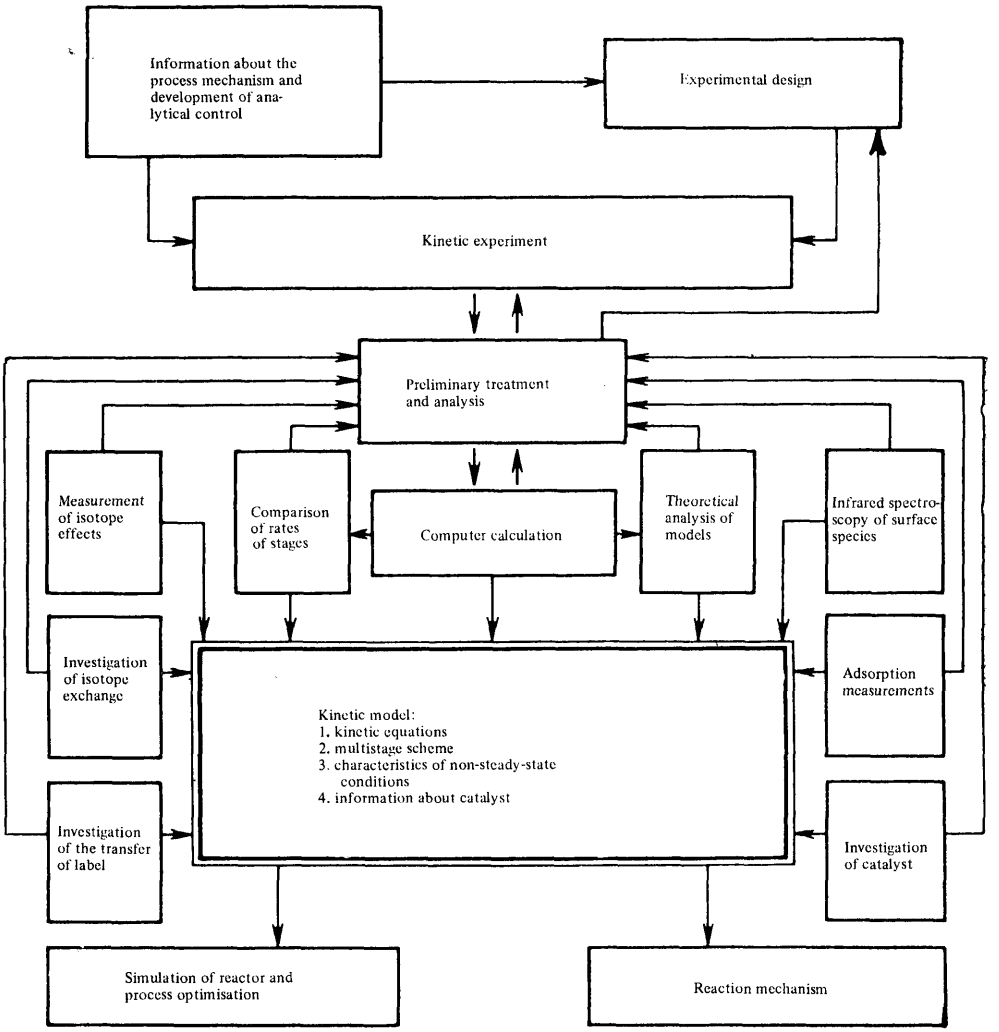
†The present authors data were obtained at higher temperatures than those of Erkelens and Ejkema[60], but, since the slow chemical adsorption stage cannot become rapid on decreasing the temperature, it is hardly likely that another stage becomes rate-limiting.

requires a physicochemical support and for this reason it is desirable to carry out complex kinetic studies in which accurate kinetic and other physicochemical measurements are combined‡.

the main ones the intermediate forms of the "blind end" compounds responsible for secondary reaction pathways (see above). Scheme 1 illustrates the formulation of complex kinetic studies. Kinetic models devised in this

Scheme 1

Formulation of complex kinetic studies



Such combination of procedures (particularly when kinetic, isotope, adsorption, and spectroscopic methods are used, especially under the conditions of the reaction investigated) may be effective in obtaining information about kinetic models. Measurements of kinetic isotope effects and the study of isotope exchange in the reaction components yield particularly valuable information about the role of the possible stages and intermediate species. On the other hand, spectroscopic studies yield more information when they are combined with kinetic measurements, which also reduces the risk of adopting as way can be justified and can be made to yield much information by making sure that the model corresponds to the specified set of results. Evidently, such models are preferable to those obtained on the basis of kinetic measurements alone.

Only a few kinetic models obtained on the basis of complex investigations are described in the literature. Some of them, described in recent publications, may be mentioned. The kinetics of the isomerisation of but-1-ene and but-2-ene in the presence of a magnesium oxide catalyst have been investigated[63] at 26°C. At the same time, a study was made of the adsorption of the reaction components and the infrared spectra of the surface species and the ESR spectra of the catalyst were obtained. The results were described by a first-order kinetic equation which was derived on the basis of a multistage mechanism

‡Here and henceforth we shall use the term "complex kinetic studies" emphasising thereby that kinetic measurements are the fundamental feature.

presupposing the physical adsorption of the initial substance with its slow conversion into the *cis*- and *trans*-isomers of but-2-ene simultaneously and their desorption.

A kinetic model for the dehydrogenation of isobutane to isobutene in the presence of an alumina–chromium oxide catalyst was obtained[64,65] in the temperature range 380 to 575°C. Apart from kinetic measurements, a study was made of the transfer of the radioactive carbon and deuterium labels[64] and a comparison was made of the rate of the process with the rate of the para-ortho conversion of hydrogen in order to determine the ratio of the rates of the stages[65]. A first-order kinetic equation satisfying the mechanism in which the slow stage is the formation of the surface compound $C_4H_{10}ads$ was obtained in both investigations.

The kinetics of the hydrogenolysis of cyclopropane in the presence of a nickel catalyst at 60°C have been investigated[66] and at the same time a study was made of the adsorption of the components and of their isotope exchange with deuterium. The rate of reaction r with formation of propane as well as ethane and methane was described by the kinetic equation

$$r = k\frac{P_1}{1 + k'P_1}, \qquad (1)$$

where P_1 is the partial pressure of the initial substance and k and k' are constants. The author justifies it by a scheme according to which a C–C bond in the adsorbed cyclopropane is dissociated on the surface with formation of adsorbed propene. The latter either combines with hydrogen (to form a surface propyl and then propane) or undergoes further hydrogenolysis to ethyl and methyl fragments.

In a study of the kinetics of the reaction of carbon monoxide and nitric oxide in the presence of copper(II) oxide at 135–200°C, i.e.

$$2CO + 2NO = 2CO_2 + N_2 \quad , \qquad (2)$$

London and Bell[67] also obtained the infrared spectra of the surface species and studied the catalyst. They derived the kinetic equation

$$r = k\frac{P_{NO}}{(1 + k_1P_{NO} + k_2P_{N_2O})(1 + k_3P_{CO})}, \qquad (3)$$

which corresponds to a scheme presupposing the following transformations:

$$NO_{gas} \rightarrow NO_{ads} \rightarrow (N_{ads} + O_{ads}) \xrightarrow{+NO} \rightarrow N_2O_{gas} \rightarrow NNO_{ads} \rightarrow O_{ads} + N_2 \xrightarrow{CO} CO_2.$$

Earlier, Apel'baum and Temkin[68] combined a careful kinetic study of the hydrogenation of ethylene on palladium with the use of the catalyst in the form of a membrane permeable to hydrogen. This enabled them to describe the kinetic data in terms of a scheme involving the interaction of the adsorbed ethylene with gaseous hydrogen followed by the slow interaction of the surface ethyl radical with adsorbed atomic hydrogen (Twigg's mechanism).

Many models devised by the present author and his coworkers for different classes of gas-reactions will be briefly considered below mainly from the standpoint of the information obtained for the construction of models from a combination of exact kinetic studies in gradient-free systems with other physicochemical methods. Kinetic equations were derived for the resulting multistage mechanisms using hypotheses concerning processes on inhomogeneous catalytic surfaces[1].

III. KINETIC MODELS OF CERTAIN REACTIONS OBTAINED BY COMPLEX INVESTIGATIONS

1. Hydrogenation Reactions

(a) Selective Hydrogenation of Diolefins. The investigations were based on the hydrogenation of isoprene to isopentenes in the presence of a palladium–lead catalyst at 58–118°C.[69-71]. The rate of reaction r is described by the equation

$$r = kP_1^{0.5}P_{H_2}, \qquad (4)$$

where P_1 and P_{H_2} are the partial pressure of the substance hydrogenated and hydrogen respectively. This equation is valid for the formation of each isopentene isomer separately, so that products with different structures arise from intermediate species without a subsequent bond redistribution. This is confirmed by the finding that, when isoprene reacts with deuterium, the degree of isotope exchange in the resulting isopentenes is slight {there is only a small amount of substituted $[D_1]$ and $[D_3]$ derivatives apart from the main addition $[D_2]$ product}. In this case kinetic isotope effects amount to 1.5–1.6, which indicates the involvement of hydrogen in the slow stages. The degree of isotope exchange in the initial isoprene is also low: hence it follows that the formation of the semihydrogenated form cannot be rapid.

Infrared spectroscopic study of the surface compounds produced in the reaction showed that the semihydrogenated form generated is strongly retained by the main part of the surface and only a small proportion (20–30%) is converted into the hydrogenation product under the reaction conditions. Experiments on the thermal desorption of hydrogen showed that it is strongly retained by the catalyst, passing into the gas phase only at high temperatures than those used in the reaction. However, this did not permit the conclusion that only the gas-phase hydrogen reacts, but it did indicate the probable nature of the relevant pathway. The combination of results led to scheme 2.

Scheme 2

Stage	Stoichiometric numbers of stages via different pathways		
	I	II	III
1. $C_5H_{8gas} = C_5H_{8ads}$	1	1	1
2. $C_5H_{8ads} = C_5H_{7ads} + H_{ads}$(slow)	0	0	1
3. $C_5H_{8ads} + H_{2gas} = C_5H_{9ads} + H_{ads}$(slow)	1	1	0
4. $C_5H_{9ads} + H_{2gas} = C_5H_{10gas} + H_{ads}$(slow)	0	1	0
5. $C_5H_{7ads} + H_{2gas} = C_5H_{9ads}$	0	0	1
6. $C_5H_{9ads} + H_{ads} = C_5H_{10gas}$(slow)	1	0	1
7. $2H_{ads} = H_{2gas}$	0	1	0

The reaction proceeds mainly via pathways I and II, with rapid formation of a surface isoprene compound and its slow interaction with gaseous or surface hydrogen. Pathway III takes into account isotope exchange.

A kinetic equation agreeing with experimental Eqn. (4) follows from Scheme 2. The combination of Eqn. (4) and scheme 2 constitutes the kinetic model of the process.

(b) Selective hydrogenation of acetylenic compounds. Reactions of this class were studied in relation to the hydrogenation of ethynyldimethylmethanol to dimethylvinylmethanol in the presence of a palladium–lead catalyst at 143–258°C [13,72,73]:

$$(CH_3)_2C(OH)C{\equiv}CH + H_2 = (CH_3)_2C(OH)CH{=}CH_2 \quad . \qquad (5)$$

The hydroxy-group is unaffected during the reaction, so that the starting compound is henceforth designated by RC≡CH, where R = $(CH_3)_2C(OH)$. The rate of the process is described by the kinetic equation

$$r = k\frac{P_1 P_{H_2}}{(P_1 + k' P_{H_2}^{0.5})^{-2.1}} \quad . \qquad (6)$$

The specific features of this equation are reflected by the maximum in the "conversion curves"[48] relating r to the degree of conversion x. The kinetic isotope effect in the replacement of H_2 by D_2 amounts to 1.8–1.9, which indicates the involvement of hydrogen in the slow stages.

The study of the interaction of the initial alcohol with deuterium by mass-spectrometric, infrared spectroscopic, and NMR methods yielded interesting information. It was found that substitution in the hydroxyl and in the methyl group does not take place at all and the degree of exchange of α-hydrogen in the initial alcohol does not exceed 14%, being more pronounced in the resulting dimethylvinylmethanol but occurring without the involvement of the gas phase, i.e. solely as a result of the redistribution of H and D among the reaction components. Thus it follows from the isotope exchange data that the hydroxy-group in the alcohol is not subject to the influence of the surface, apparently because it is remote from the latter owing to the rigidity of the molecule. The absence of isotope exchange between the gas phase and dimethylvinylmethanol, whose molecules should no longer be rigid, shows that the latter is not retained by the surface in the presence of the initial alcohol, passing immediately to the gas phase. The small contribution of the isotope exchange involving the acetylenic alcohol shows that its interaction with hydrogen is not the rapid reaction stage.

Combination of the results leads to Scheme 3 in which the first pathway predominates:

Scheme 3

Stage	Stoichiometric numbers of stages via different pathways		
	I	II	III
1. $HC = CR_{gas} = HC = CR_{ads}$	1	1	1
2. $H_{2gas} = 2H_{ads}$	1	0	0
3. $HC = CR_{ads} + 2H_{ads} = H_2C = CHR_{gas}$(slow)	1	0	0
4. $HC = CR_{ads} + H_{2gas} = H_2C = CHR_{gas}$(slow)	0	1	0
5. $HC = CR_{ads} + H_{2gas} = HC = CHR_{ads} + H_{ads}$(slow)	0	0	1
6. $HC = CHR_{ads} + H_{ads} = H_2C = CHR_{gas}$(slow)	0	0	1

This scheme leads to a kinetic equation agreeing with experimental Eqn. (6). Evidently the kinetic models of the two reactions considered above differ significantly in the presence of the same catalyst.

(c) Hydrogenation of Aromatic Hydrocarbons. Kinetic models have been obtained[74-80] for the hydrogenation of benzene and toluene in the presence of a nickel oxide–zinc oxide catalyst at temperatures up to 270°C, mainly in the region where the processes are reversible. The rates of both reactions pass through a maximum at 180–190°C and the region where the reactions are reversible corresponds to the descending sections of the r–T curves, the decrease of the reaction rate with increasing temperatures being unrelated to the approach to equilibrium and being caused by the process mechanism. The kinetics of the two reactions in the region of reversibility are described by the equation

$$r = kP_1^{0.5} P_{H_2}^2 \gamma, \qquad (7)$$

where γ is the multiplier taking into account the influence of the reverse reaction[81]. Kinetic equations for the forward[82] and reverse[83-85] processes have been obtained separately for the hydrogenation of benzene, the equation for the reverse reactions being

$$r = kP_{C_6H_{12}} P_{C_6H_6}^{-0.5}. \qquad (8)$$

In the region of low conversions at low pressures $P_{C_6H_{12}}$ (up to 0.1 atm) another equation is valid for the rate of dehydrogenation of cyclohexane:

$$r = kP_{C_6H_{12}}^{0.5}, \qquad (9)$$

with increase of the partial pressure of C_6H_{12}, it is converted into a zero-order equation.

Comparison of the rates of hydrogenation of [^{14}C] benzene, cyclohexene, and cyclohexadiene (separately or jointly)[61] showed that, over the entire range of conversions, benzene reacts much more slowly, so that the transformations of C_6H_8 and C_6H_{10} in the hydrogenation of benzene cannot constitute the slow stage. Under these conditions, the rate of hydrogenation of cyclohexene in the presence of an excess of hydrogen is expressed by the equation

$$r = kP_{C_6H_{10}} P_{C_6H_{12}}^{-0.5}. \qquad (10)$$

Comparison with the rate of the para-ortho conversion of hydrogen

$$para\text{-}H_2 = ortho\text{-}H_2 \qquad (11)$$

under analogous conditions yields information about the contribution of the rates of adsorption and desorption of hydrogen to the overall rate of the process. It was found that the rates of hydrogenation of benzene and dehydrogenation of cyclohexane are much lower than the rate of reaction (11); consequently the adsorption and desorption of hydrogen cannot be the slow stages in the given process.

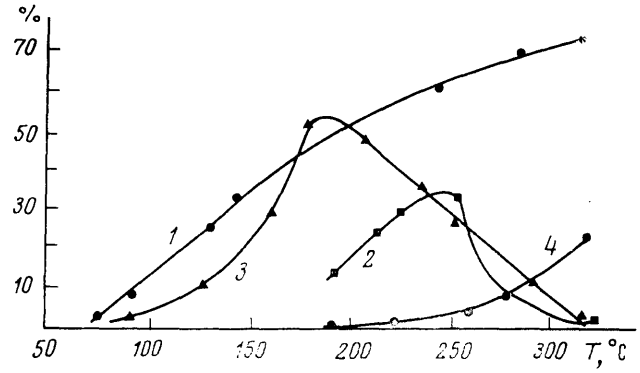


Figure 1. Temperature dependence of the degree of conversion in hydrogen–deuterium isotope exchange processes in benzene (curve *1*) and cyclohexane (curve *2*), the hydrogenation of benzene (curve *3*), and the dehydrogenation of cyclohexane (curve *4*) in the presence of a nickel oxide–zinc oxide catalyst.

Figs. 1–3 present the temperature variation of the rate of isotope exchange (proportional to the degree of conversion) between hydrogen and deuterium in the initial substances and in the products of the given reactions. Evidently, the rate of isotope exchange in benzene and toluene increases monotonically with temperature and

greatly exceeds the rate of hydrogenation. On the other hand, the rate of dehydrogenation increases with temperature, while that of isotope exchange passes through a maximum, although in the region of the reversibility of the reaction it exceeds the rate of dehydrogenation. The rates of hydrogenation and dehydrogenation of cyclohexane are much higher than the rate of isotope exchange, which is extremely low.

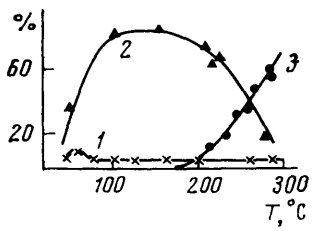


Figure 2. Temperature dependence of the degree of conversion in hydrogen–deuterium isotope exchange processes in cyclohexene (curve *1*), the hydrogenation of cyclohexene (curve *2*), and its dehydrogenation (curve *3*) in the presence of a nickel oxide–zinc oxide catalyst.

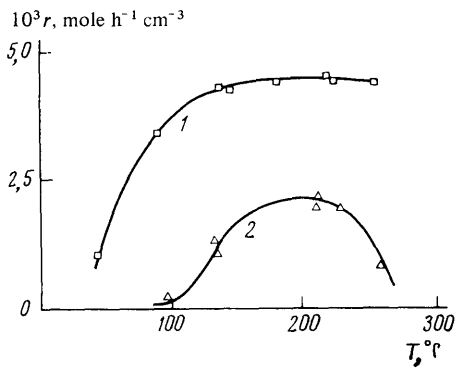


Figure 3. Temperature dependence of the rate of the hydrogen–deuterium isotope exchange in toluene (curve *1*) and the hydrogenation of toluene (curve *2*) in the presence of a nickel oxide–zinc oxide catalyst.

The exchange in toluene proceeds most readily when the methyl group is involved; the nature of the isotope distribution in the methylcyclohexane shows that the latter is not retained by the catalyst surface. Comparison of the rates of the ortho-para conversion of hydrogen on the clean catalyst surface and on the surface with adsorbed cyclohexane or cyclohexene [86] confirms the dissociative mechanism of the adsorption of cyclohexane. The study of the adsorption of benzene [87], the infrared spectra of the surface compounds, and ferromagnetic resonance [88,89] as well as quantum-chemical calculations [90] led to the conclusion that the benzene molecules assume a planar orientation with the probable formation of π-complexes. These results made it possible to rule out the possibility of slow adsorption and desorption stages in the hydrogenation of benzene and cyclohexane.

Measurements of the kinetic isotope effects β confirmed these conclusions. Table 3 lists the values of β obtained, expressed as the ratios k_H/k_D of the rate constants for the reactions before and after the substitution of protium by deuterium (the values of β may be distorted slightly owing to isotope exchange during the reaction).

Table 3. Kinetic isotope effects β in the substitution of H by D in the hydrogenation of benzene, cyclohexene, and toluene and in the dehydrogenation of cyclohexene.

T, °C	Reaction	β	T, °C	Reaction	β
240	$C_6H_6+3H_2=C_6H_{12}$ $C_6D_6+3H_2=C_6D_6H_6$	0.53	110	$C_6H_{10}+H_2=C_6H_{12}$ $C_6H_{10}+D_2=C_6H_{10}D_2$	0.99
240	$C_6H_6+3H_2=C_6H_{12}$ $C_6H_6+3D_2=C_6H_6D_6$	0.60	220	$C_6H_{10}+H_2=C_6H_{12}$ $C_6H_{10}+D_2=C_6H_{10}D_2$	1.02
240	$C_6D_6+3H_2=C_6H_6D_6$ $C_6D_6+3D_2=C_6D_{12}$	0.55	217	$C_6H_5CH_3+3H_2=C_7H_{14}$ $C_6H_5CH_3+3D_2=C_7H_8D_6$	0.39
240	$C_6H_6+3H_2=C_6H_{12}$ $C_6D_6+3D_2=C_6D_{12}$	0.28	217	$C_6H_5CH_3+3H_2=C_7H_{14}$ $C_6D_5CH_3+3H_2=C_7D_5H_9$	0.92
270	$C_6H_6+3H_2=C_6H_{12}$ $C_6H_6+3D_2=C_6H_6D_6$	0.51	217	$C_6H_5CH_3+3H_2=C_7H_{14}$ $C_6H_5CD_3+3H_2=C_6H_{11}CD_3$	1.10
293	$C_6H_{12}=C_6H_6+3H_2$ $C_6D_{12}=C_6D_6+3D_2$	2.3	217	$C_6H_5CH_3+3H_2=C_7H_{14}$ $C_6D_5CD_3+3H_2=C_7D_8H_6$	0.77
265	$C_6H_{12}=C_6H_6+3H_2$ $C_6D_{12}{}^*=C_6D_6+3D_2$	1.8	217	$C_6H_5CH_3+3H_2=C_7H_{14}$ $C_6D_5CD_3+3D_2=C_7D_{14}$	0.89
			250	$C_6H_6CH_3+3H_2=C_7H_{14}$ $C_6D_5CD_3+3H_2=C_7D_8H_6$	0.59

*A mixture of different deuterocyclohexanes.

Appreciable effects in the hydrogenation of benzene and toluene involving the replacement of protium by deuterium in the hydrocarbon and in the hydrogen molecule indicate the involvement of the two components in the slow stages. It is remarkable that the effects observed here are the opposite of those usually found (the rate of the process increases following substitution by the heavy isotope instead of decreasing in accordance with the postulate of the elementary theory of isotope effects [91–93]; on the other hand, the effects in the reverse reaction are normal). The present author explained this finding on the basis of the multistage nature of the process and the relative bond strengths in the initial substances and in the activated complexes [94].

The stoichiometric number ν of the rate-limiting stage [1,4,5] was calculated from the values of β for the forward and reverse reactions by Boreskov's method [95]. It proved to be unity, which rules out the possibility that the reaction proceeds via slow stages characterised by other stoichiometric numbers (for example, the absorption of hydrogen or a process proceeding via the disproportionation of intermediates [1,96]). Table 3 shows that there is no isotope effect in the hydrogenation of cyclohexene; consequently, hydrogen is not involved in the slow stage. The slow stage can only be the formation of a surface cyclohexene compound, which is also confirmed by isotope exchange data (see above).

Comparison of the rates of hydrogenation and isotope exchange for benzene and its alkyl derivatives showed that the rate of hydrogenation decreases steadily, while that of isotope exchange remains at approximately the same level. On the other hand, in cycloalkanes it depends significantly on the nature of the substitution [79,97].

A scheme for the hydrogenation of benzene and toluene, providing for the rapid formation of a surface π-complex of the hydrocarbon on the part of the surface weakly retaining molecularly adsorbed hydrogen, which does not hinder the adsorption of the hydrocarbon, was put forward on the basis of the complete set of results. Subsequently, there is slow interaction between the hydrocarbon and the surrounding molecules of the weakly bound hydrogen, which leads to the formation of a coordination complex retaining the features of a surface π-complex. This reaction stage virtually constitutes a rearrangement of the surface bonds. The complex formed undergoes rapid isomerisation as far as the cycloalkane (possibly also via other intermediate stages), as shown in Scheme 4.

Scheme 4

1. $H_2 = (H_2)_{ads}$
2. $C_nH_{2n-6} + (Ni) = C_nH_{2n-6}(Ni)$
3. $C_nH_{2n-6}(Ni) + 3(H_2)_{ads} = [C_nH_{2n-6}(Ni)] \cdot 3H_2$ (slow)
4. $[C_nH_{2n-6}(Ni)] \cdot 3H_2 = [C_nH_{2n-4}(Ni)] \cdot 2H_2$ (rapid isomerisation)
5. $[C_nH_{2n-4}(Ni)] \cdot 2H_2 = [C_nH_{2n-2}(Ni)] \cdot H_2$ (rapid isomerisation)
6. $[C_nH_{2n-2}(Ni)] \cdot H_2 = C_nH_{2n\,gas} + (Ni)$.

The isotope exchange in benzene and toluene under the conditions of their hydrogenation also proceeds via the formation of a π-complex, which is converted, in conformity with the dissociative π-complex substitution mechanism[98], into a σ-bonded intermediate compound with elimination of a hydrogen atom (H_{ads}).

Scheme 4 leads to kinetic equations agreeing with the experimental Eqns. (7)–(9). Analysis shows that the decrease of the reaction rate after the temperature maximum and the formally negative apparent activation energies obtained are due to the high heats of formation of the surface compounds (their estimate[99] for benzene gave values in the range 25–35 kcal mole^{-1}).

In the region of irreversibility, the rate of hydrogenation of benzene is described by other relations: the equation

$$r = kP_{H_2}^{0.5} \tag{12}$$

holds at 90–135°C, while the equation

$$r = kP_1P_{H_2} \tag{12a}$$

is valid in the range 150–180°C. Here the process mechanism changes significantly and the rate of reaction is apparently determined by the rate of formation of the intermediate compounds $C_6H_7(Ni)$ and $C_6H_8(Ni)$ respectively.

The following kinetic equation is valid for the reaction in the presence of a nickel oxide–chromium oxide catalyst under the same conditions[100]:

$$r = kP_1^nP_{H_2}^m; \quad m = 1.5 - 1.2; \quad n = 0 - 0.5. \tag{13}$$

According to the authors[100], this corresponds to reaction via six slow stages involving consecutive addition of hydrogen and follows from a more general complex equation.

Thus the examples presented show that the kinetic models for the hydrogenation of organic compounds of different classes are distinguished by high specificity and a wide variety.

2. Isotope Exchange Reactions Involving Hydrocarbons

A kinetic model has been obtained[101-103] for isotope exchange reactions between hydrogen and deuterium in cyclohexane in the presence of nickel and platinum at low temperatures (up to 80°C). Previously, exact kinetic models for isotope exchange in hydrocarbons had been altogether absent from the literature. It was found that in the presence of nickel catalysts there is a possibility of two exchange mechanisms depending on the surface concentration of deuterium. In the presence of an excess of the latter, products with low degrees of substitution are formed, while in the presence of its deficiency mainly highly deuterated products are generated. The intermediate species responsible for isotope exchange in cyclohexane and benzene and for the hydrogenation of benzene were found to be different, i.e. the exchange in cyclohexane does not proceed via aromatic intermediates. In contrast to isotope exchange, the hydrogenation of benzene on nickel hardly occurs in the absence of hydrogen (deuterium) in the gas phase, i.e. the process requires the presence of weakly bound hydrogen (this can also be regarded as confirmation of the hydrogenation mechanism proposed above[4]). The rate of isotope exchange

$$C_6H_{12} + yD_2 = C_6H_{12-y}D_y + yHD, \quad y = 1, 2, \ldots, 12, \tag{14}$$

at low pressures and temperatures is described by the kinetic equation

$$r = k\frac{P_1P_{D_2}^{0.5}}{(k_1P_1 + k_2P_{D_2}^{0.5})^2}, \tag{15}$$

which holds both for the overall exchange and for the initial rates of formation of each product with different constants k. This is illustrated in Fig. 4, which shows that the rate of accumulation of each product constitutes a constant fraction of the rate of consumption of C_6H_{12}. Calculation of the isotope distribution in the products by a stochastic method yields values agreeing with experimental data only if simultaneous (and not consecutive) formation of all the substitution products in the initial stages of the processes is postulated (see Fig. 5).

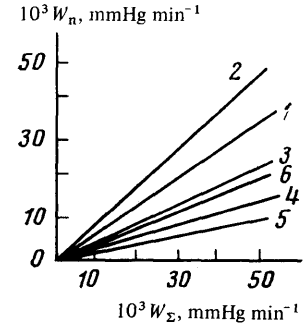


Figure 4. Dependence of the rates of accumulation W_n of different $[D_n]$ deuterocyclohexanes on the rate W_Σ of consumption of $[D_0]$ cyclohexane at 30°C in the presence of platinum: 1)–6) curves for the accumulation of $[D_1]$–$[D_6]$-cyclohexanes respectively.

The proposed scheme (Scheme 5) provides for the formation of all the products via the successive abstraction of hydrogen from the surface fragment on interaction with surface D atoms (for simplicity, it covers only the range y = 1–6). The formation of each product is described by the corresponding stoichiometric reaction pathway.

Scheme 5 alsc explains the different types of isotope distribution in the exchange products on nickel and platinum. This is due to the different ratios of the rates of reaction via pathway I and the remaining pathways, depending on the rates of stages 4 and 14.

Scheme 5*

Stage	Stoichiometric numbers of stages via different pathways					
	I	II	III	IV	V	VI
1. $D_2 = 2D_{ads}$	1	2	3	4	5	6
2. $C_6H_{12} = C_6H_{12ads}$	1	1	1	1	1	1
3. $C_6H_{12ads} + D_{ads} = C_6H_{11ads} + \underline{HD}$	1	1	1	1	1	1
4. $C_6H_{11ads} + D_{ads} = C_6H_{10ads} + \underline{HD}$	0	1	1	1	1	1
5. $C_6H_{10ads} + D_{ads} = C_6H_{10}D_{ads}$	0	1	1	1	1	1
6. $C_6H_{10}D_{ads} + D_{ads} = C_6H_9D_{ads} + \underline{HD}$	0	0	1	1	1	1
7. $C_6H_9D_{ads} + D_{ads} = C_6H_9D_{2ads}$	0	0	1	1	1	1
8. $C_6H_9D_{ads} + D_{ads} = C_6H_8D_{2ads} + \underline{HD}$	0	0	0	1	1	1
9. $C_6H_8D_{2ads} + D_{ads} = C_6H_8D_{3ads}$	0	0	0	1	1	1
10. $C_6H_8D_{3ads} + D_{ads} = C_6H_7D_{3ads} + \underline{HD}$	0	0	0	0	1	1
11. $C_6H_7D_{3ads} + D_{ads} = C_6H_7D_{4ads}$	0	0	0	0	1	1
12. $C_6H_7D_{4ads} + D_{ads} = C_6H_6D_{4ads} + \underline{HD}$	0	0	0	0	0	1
13. $C_6H_6D_{4ads} + D_{ads} = C_6H_6D_{5ads}$	0	0	0	0	0	1
14. $C_6H_{11ads} + D_{ads} = \underline{C_6H_{11}D}$	1	0	0	0	0	0
15. $C_6H_{10}D_{ads} + D_{ads} = \underline{C_6H_{10}D_2}$	0	1	0	0	0	0
16. $C_6H_9D_{2ads} + D_{ads} = \underline{C_6H_9D_3}$	0	0	1	0	0	0
17. $C_6H_8D_{3ads} + D_{ads} = \underline{C_6H_8D_4}$	0	0	0	1	0	0
18. $C_6H_7D_{4ads} + D_{ads} = \underline{C_6H_7D_5}$	0	0	0	0	1	0
19. $C_6H_6D_{5ads} + D_{ads} = \underline{C_6H_6D_6}$	0	0	0	0	0	1

*Compounds evolved into the gas phase are underlined; stages 3–19 are assumed to be slow. Pathways VII–XII have been omitted for brevity as well as the subsequent stages 20, 21, ...

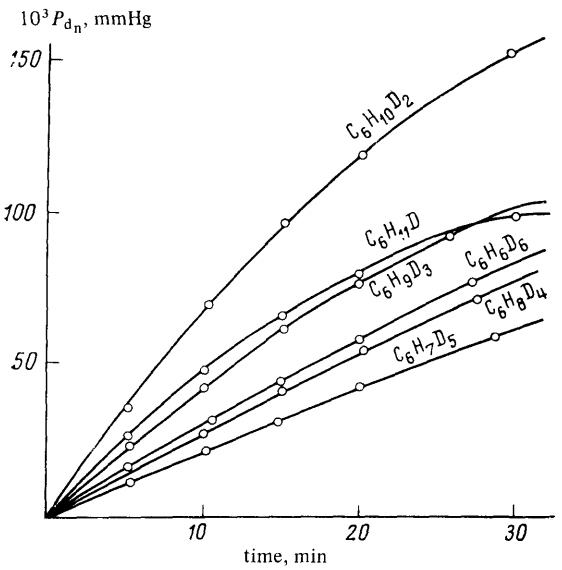


Figure 5. Time dependence of the distribution of isotopes in the products of the exchange between cyclohexane and deuterium at 30°C in the presence of nickel. The curves were calculated from the probable distribution based on the initial rates of formation of $[D_n]$cyclohexanes and the circles represent the experimental partial pressures of different $[D_n]$ cyclohexanes.

The model obtained actually relates for the first time the kinetics of the exchange in hydrocarbons to the nature of the isotope distribution and the mechanism of these multipathway reactions.

3. Dehydrogenation Reactions

The dehydrogenation of isopropyl alchol to acetone in the presence of nickel has been investigated in detail[104–106] in the region corresponding to the reversibility of the reaction (130–200°C):

$$iso\text{-}C_3H_7OH = CH_3COCH_3 + H_2. \quad (16)$$

Although this reaction has been frequently used by various investigators as a model, there were virtually no accurate kinetic literature data for this process. The kinetics of the reaction proved to be extremely unusual. The reaction is inhibited by one of the products (acetone), but is appreciably accelerated by the other (hydrogen), the rate of the process, measured in accordance with a single-parameter scheme[50], being proportional to the alcohol concentration. Fig. 6 compares the rates of dehydrogenation and isotope exchange in the alcohol and acetone.

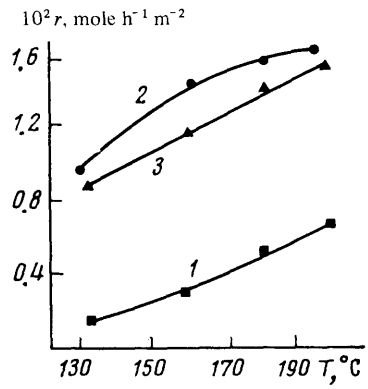


Figure 6. Temperature dependence of the rates of dehydrogenation of isopropyl alcohol (curve *1*) and the hydrogen–deuterium isotope exchange in isopropyl alcohol (curve *2*) and acetone (curve *3*) in the presence of nickel.

The rate of the overall isotope exchange in the alcohol exceeds approximately by a factor of three the rate of dehydrogenation, which is approximately the same as the rate of isotope exchange involving the hydrogen of the hydroxy-group. The nature of the isotope distribution in the exchange products (according to infrared and NMR spectra) and the results of the measurements of the kinetic isotope effects quoted below show that there is no intermediate enol rearrangement in this instance. Table 4 lists the kinetic isotope effects β for the replacement of protium by deuterium in the forward and reverse processes of the acetone hydrogenation reaction:

$$CH_3COCH_3 + H_2 = iso\text{-}C_3H_7OH; \quad (17)$$

here β is defined as the ratio of the rates of reactions involving compounds with the light (r_H) and heavy (r_D) isotopes under the same initial conditions and for the same composition of the reaction mixture:

$$\beta = r_H/r_D. \quad (18)$$

Table 4 shows that there is virtually no isotope effect in the substitution of protium by deuterium in the alkyl group of the alcohol, but it is appreciable for substitution in the hydroxy-group. This can be regarded as proof that the hydrogen of the hydroxy-group is involved in the slow stage (confirming the isotope exchange data) and that the adsorption and desorption stages are rapid.

Table 4. Kinetic isotope effects β in the dehydrogenation of isopropyl alcohol and the hydrogenation of acetone on nickel at 200°C.

Reaction	β	Reaction	β
$C_3H_7OH=C_3H_6O+H_2$ $C_3H_7OD=C_3H_6O+HD$	3.4	$C_3H_6O+H_2=C_3H_7OH$ $C_3D_6O+H_2=C_3D_6HOH$	1.0
$C_3H_7OH=C_3H_6O+H_2$ $C_3D_7OH=C_3D_6O+HD$	1.1	$C_3H_6O+H_2=C_3H_7OH$ $C_3H_6O+D_2=C_3H_6DOD$	0.8
$C_3H_7OH=C_3H_6O+H_2$ $C_3D_7OD=C_3D_6O+D_2$	4.3	$C_3H_6O+H_2=C_3H_7OH$ $C_3D_6O+D_2=C_3D_7OD$	0.8
		$C_3H_7OH=C_3H_6O+H_2$ (in excess of H_2) $C_3H_7OH=C_3H_6O+H_2$ (in excess of D_2)	3.5

The marked isotope effect in the replacement of the excess hydrogen by deuterium in the dehydrogenation of isopropyl alcohol confirms the involvement of hydrogen, in conformity with kinetic data. The observed low values of the isotope effects ($\beta < 1$) in reaction (17) are due to its specific features, which are analogous to those mentioned above for the hydrogenation of aromatic hydrocarbons. Comparison of the rate of reaction (16) with that of reaction (11) under the same conditions also demonstrated the impossibility of slow hydrogen desorption and adsorption stages.

The set of the above data corresponds to the following two-pathway scheme (Scheme 6), which provides for the simultaneous occurrence of the process via the slow abstraction of the hydrogen of the hydroxy-group directly from the adsorbed alcohol, which predominates at high concentrations of surface hydrogen:

Scheme 6

Stage	Stoichiometric numbers of the stages via different pathways	
	I	II
1. $H_2 = 2H_{ads}$	1	0
2. $CH_3CH(OH)CH_{3gas} = CH_3CH(OH)CH_{3ads}$	1	0
3. $CH_3CH(OH)CH_{3ads} = CH_3CH(O)CH_{3ads} + H_{ads}$(slow)	1	0
4. $CH_3CH(OH)CH_{3gas} + H_{ads} = CH_3CH(O)CH_{3ads} + H_2$(slow)	0	1
5. $CH_3CH(O)CH_{3ads} = CH_3COCH_{3ads} + H_{ads}$	1	1
6. $CH_3COCH_{3ads} = CH_3COCH_{3gas}$	1	1

With increase of the concentration of surface hydrogen, hydrogenation proceeds mainly as a result of the slow interaction of the gaseous alcohol with the surface hydrogen.

The kinetic equation giving the best (compared with all the other equations which have been tested) description of the experimental data follows from the scheme:

$$r = k\frac{P_1(1+k^*P_{H_2}^{0.5})\gamma}{1+k_1P_{ac}+k_2P_{ac}P_{H_2}^{0.5}+k_3P_{H_2}^{0.5}}, \quad (19)$$

where P_{ac} is the partial pressure of acetone and γ a correction for the influence of the reverse reaction (the unity in the denominator may not be neglected only for the description of the initial stage of the reaction for very low values of P_{ac}). Evidently the accelerating effect of hydrogen can be naturally accounted for within the framework of this scheme: it can be retained by the surface either during reduction or in the course of the reaction. A similar behaviour has been observed in the dehydrogenation of cyclohexane [107-109] and isopentenes [110] on palladium.

The above results also make it possible to characterise the kinetic model for the hydrogenation of acetone [111]. It corresponds to the reverse of Scheme 6 and the equation

$$r = k\frac{P_{ac}P_{H_2}(1+k^*P_{H_2}^{0.5})\gamma}{1+k_1P_{ac}+k_2P_{ac}P_{H_2}^{0.5}+k_3P_{H_2}^{0.5}}. \quad (20)$$

In the region corresponding to irreversibility, the rate of reaction (17) at lower temperatures (up to 90°C) is described by another equation according to Babkova et al. [112]:

$$r = k\frac{P_{ac}P_{H_2}}{(1+k_1P_{ac}+k_2P_{ac}P_{H_2}^{0.5}+k_3P_{al})(1+k'P_{H_2}^{0.5})}, \quad (21)$$

while in the presence of a copper catalyst it is described by the equation

$$r = k\frac{P_{ac}^2P_{H_2}}{(1+k_1P_{ac}+k_2P_{ac}P_{H_2}^{0.5}+k_3P_{al})^2} \quad (22)$$

(P_{al} is the partial pressure of the alcohol).

Thus the complex kinetic investigation of the dehydrogenation of isopropyl alcohol in the presence of nickel in the region of reversibility made it possible to obtain concordant results and to elucidate the complex pattern of the reaction, which had been previously regarded as extremely simple. Conclusions concerning the characteristics of this process cannot, however, be extended to other dehydrogenation reactions. Thus quite different results were obtained [113-115] in a complex investigation of the selective dehydrogenation of cyclohexanol to cyclohexanone in the presence of a copper–magnesium catalyst at 210–270°C:

$$C_6H_{11}OH = C_6H_{10}O + H_2 \quad . \quad (23)$$

This shows that there are differences between the kinetic models. The rate of reaction (23) no longer depends on the concentration of hydrogen and there is no proportionality between the rate of the process and the concentration of the starting material, but inhibition by the ketone is also observed. The results of the measurements of the kinetic isotope effects for the forward and reverse processes are listed in Table 5.

Table 5. Kinetic isotope effects β in the dehydrogenation and hydrogenation of cyclohexanol at 240°C.

Reaction	β
$C_6H_{11}OH=C_6H_{10}O+H_2$ $C_6H_{11}OD=C_6H_{10}O+HD$ $C_6H_{11}OD=C_6H_9DO+H_2$	1.0
$C_6H_{11}OH=C_6H_{10}O+H_2$ (in excess of H_2) $C_6H_{11}OH=C_6H_{10}O+H_2$ (in excess of D_2)	1.0
$C_6H_{10}O+H_2=C_6H_{11}OH$ $C_6H_{10}O+D_2=C_6H_{10}DOD$	1.3

Evidently there is no isotope effect in the substitution of the hydrogen in the hydroxy-group and when the reaction is carried out in an atmosphere of deuterium, but it does operate in the reverse reaction. Experiments on isotope

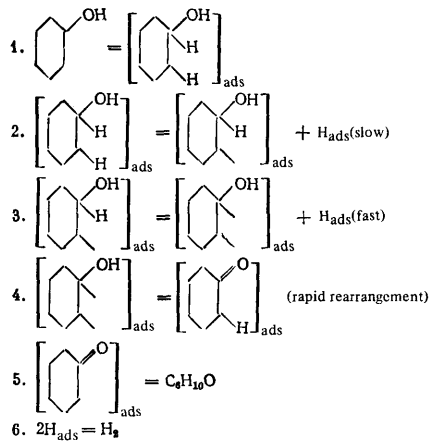
exchange showed that the rate of exchange of the hydroxyl hydrogen is higher than the rate of the reaction itself.

The rate of reaction (23) corresponds to Scheme 7 and the following kinetic equation:

$$r = k\frac{P_1\gamma}{(P_1 + k'P_{ket})^m}, \quad m = 0.5 - 0.6, \tag{24}$$

where P_{ket} is the partial pressure of cyclohexanone. Scheme 7 presupposes the occurrence of the reaction via the slow abstraction of β-hydrogen and rapid enol rearrangement.

Scheme 7



Thus a change in the structure of the molecule and the use of a different metallic catalyst have a significant influence on the form and properties of the kinetic model, while the general character of the reaction remains the same. The kinetic models for the dehydrogenation of hydrocarbons have a completely different form [116-118]. This shows yet again that dehydrogenation processes cannot be embraced by a general kinetic model, as suggested previously by some workers.

4. Extensive Oxidation of Microadmixtures of Organic Substances

These reactions were investigated in relation to the oxidation of microadmixtures of n-pentane, benzene, and their mixtures [119,120] in the presence of an aluminium-platinum [alumina-platinum?] catalyst and platinum foil at 100-350°C over a wide range of conditions. The rate of extensive oxidation of benzene is expressed by the equation

$$r = \frac{kP_1P_{O_2}^{0.5}}{(1 + k_1P_1 + k_2P_1P_{O_2}^{0.5} + k_3P_{H_2O}P_{O_2}^{-0.5})^2}; \tag{25}$$

at fairly high oxygen concentrations ($P_{O_2} \geq 0.1$ atm), we have

$$r = kP_1/(1 + k'P_1)^2. \tag{26}$$

At 130°C and above, a heterogeneous-homogeneous process mechanism operates to some extent (this was demonstrated by the inhibiting effect of the packing in a reactor with a vibrofluidised catalyst bed[121] and directly by the method involving separate calorimetric measurements [122]), which leads to the appearance of additional terms in Eqns. (25) and (26). This is a fairly rare instance; the homogeneous propagation of the oxidation reactions of organic compounds (which is in general not observed very frequently) usually occurs only at 400-600°C [123,124]. Above 240°C, the reaction passes to the external-diffusion region. When benzene is replaced by deuterobenzene, there is no kinetic isotope effect, so that the slow stages of the process apparently do not entail the dissociation of C-H bonds. The mechanism of the process presupposes its simultaneous occurrence via four independent pathways: the purely heterogeneous pathway (via successive oxidative cracking on the surface of platinum coated with oxygen with slow stages involving the conversion of aromatic bonds into ordinary bonds), the heterogeneous-homogeneous pathway (with transfer of the intermediate oxygen complexes of benzene into the gas phase and their subsequent interaction with molecular oxygen) and two "empty" pathways involving the deactivation of radical-like compounds in the gas phase.

The characteristics of the extensive oxidation of n-pentane are quite different; there is no homogeneous propagation of the reaction and the kinetic isotope effects show that the slow stages involve the dissociation of C-H bonds, the rate of the process being described by the equation

$$r = kP_1, \tag{27}$$

which corresponds to a scheme presupposing slow dissociative adsorption of pentane on the oxidised surface of platinum.

When both hydrocarbons are oxidised simultaneously, pentane does not affect the oxidation of benzene; at low concentrations, benzene does not affect the oxidation of pentane up to a certain critical concentration beyond which benzene causes a sharp inhibition of the pentane oxidation reaction. The rate of oxidation of pentane in the presence of benzene is characterised by the equation

$$r = k\frac{P_1}{(1 + k'P_{C_6H_6})^2}, \tag{28}$$

corresponding to kinetic models involving separate oxidation processes.

The above examples show that accurate complex investigations lead to exceptionally varied and specific kinetic models for different classes of reactions and catalysts.

IV. NON-STEADY-STATE KINETIC MODELS

The kinetic models discussed above characterise steady-state or quasi-steady-state reactions. The concentrations of the intermediates formed and decomposed during the process then remain constant under specified conditions, corresponding to the given constant concentrations of the reactants, and when the latter are altered, there is sufficient time for new concentrations of the intermediates corresponding to them to be established. Steady-state conditions can frequently break down, so that the catalytic reactions proceed as non-steady-state processes. Such breakdown is caused, particularly, by the activation of the catalyst in the initial stages of the reactions, by the gradual blocking of the surface by side products, by the influence of the reaction system, by the changes associated with transitions to other conditions, and by other factors causing oscillations or steady alterations in the activity of the catalysts [125-127].

Analysis demonstrates the possibility of the occurrence of more than one steady state of the process in the kinetic region, depending on its mechanism and the nature of the

kinetic model[128-132]. The necessary condition for this is the presence of stages involving interaction between different intermediates[128-132,164-166]. A multiplicity of steady states has been observed experimentally, for example, in the reaction of carbon monoxide with hydrogen in the presence of nickel[141].

The attainment of a steady state requires a certain relaxation time of the rate of reaction[126,133,167,168]. In conformity with Frank-Kamenetskii's conditions[169], it must be much shorter than the reaction time and must depend on the conditions of the process, its mechanism, and the ratios of the rates in different stages (Belousov[170] refers to the relaxation time as the duration of the intrinsically non-steady state). Temkin[126,167,168] showed that the relaxation time constitutes in the general case a fraction of the "reaction turnover time", which is the reciprocal of the "reaction turnover number"[41] (i.e. the number of molecules which have reacted per unit time referred to the number of active sites on the catalyst surface).

The relaxation time characterises the time required for the attainment of the steady state, determined by the specific features of the multistage nature of the process and its mechanism, but not by other influences caused by the effect of the reaction system on the catalyst and secondary factors. Relaxation in consequence of such "secondary influences"[126,168] may be much more prolonged than the reaction itself and the process as a whole then takes place under non-steady-state conditions. Such a situation arises, for example, in the oxidation of ethylene in the presence of silver[171] owing to the modifying effect of the oxygen penetrating into the surface layer of the catalyst.

Experimental studies on processes under non-steady-state conditions, both in order to determine the relaxation time as a function of various factors and to elucidate other characteristics, can therefore serve as an effective means for devising kinetic models required for a more complete understanding of catalytic processes. Certain approaches of this kind have been described in the literature, for example, in Refs. 42, 43, 133–139, and 172–175. Thus the determination of the ignition limits in the synthesis of alcohols on transition of the latter from the kinetic region to the external-diffusion region has been used to describe the rate of this process[133]. The study of decay phenomena as a function of various factors in the transition of the ammonia oxidation reaction on a non-platinum catalyst from the external-diffusion to the kinetic region made it possible to derive a kinetic equation for the reaction[139]. Non-steady-state effects in the ammonia and sulphur dioxide oxidation reactions have been investigated[174,175] by the electrothermographic method. The parameters of the non-steady-state kinetic models for the oxidation of carbon monoxide on platinum and lanthanum trioxide have been determined and the models have been analysed[128,176,177]. The kinetics of the oxidation of hydrogen in the presence of nickel under the conditions of stable auto-oscillations of the system, having a chemical mechanism, have been investigated by Slin'ko and coworkers[142,178,179].

Non-steady-state kinetic models have also been obtained for the hydrochlorination of acetylene[143], the oxidation of propene, and its oxidative ammonolysis[144]. For a model of this kind, Gel'bshtein and coworkers[144] reported to the earlier idea[180] of a surface "reaction layer" of the catalyst, where oxygen ionises and is transferred from centres of one type to those of another. They believe[144] that the thickness of this layer determines the occurrence of the process under particular conditions. When the layer is thin, the characteristics of the steady-state and non-steady-state course of the reaction are the same. Many non-steady-state kinetic models have been devised for the description of the dehydrogenation of hydrocarbons, taking into account the blocking of the catalyst by coke[116,117,145-147,181-183] (although not all such models have been adequately justified). The earlier models for the dehydrogenation of hydrocarbons containing four carbon atoms in the presence of alumina–chromium oxide catalysts have been reviewed[184].

A kinetic model (unsupported by multistage mechanisms), taking into account the rates of conversion of butane into butenes (r_1) and of butenes into butadiene (r_2), of the cracking of butane (r_3), and of coke formation from both hydrocarbons (r_4 and r_5) has been proposed for the single-stage dehydrogenation of butane in the presence of an alumina–chromium oxide catalyst in the temperature range 570–630°C [145]:

$$r_1 = k_1(1 - c/c_{max})P_1\gamma/M^2, \quad (29)$$

$$r_2 = k_2(1 - c/c_{max})^2 P_{C_4H_8}\gamma/M^2, \quad (30)$$

$$r_3 = k_3(1 - c/c_{max})P_1/M, \quad (31)$$

$$r_4 = k_4 P_{C_4H_8}/M^2, \quad (32)$$

$$r_5 = k_5 P_{C_4H_8}/M^2, \quad (33)$$

where M depends on the concentrations of all the reactants and the rate of the main reactions depends on the area of the coke-free surface (c and c_{max} are the concentration of coke at any instant and the concentration corresponding to monolayer coverage).

The dependence of the rate of the process on the amount of coke and the influence of the oxygen concentration ω in the surface layer of the catalyst, which varies owing to the slow diffusion of oxygen during preliminary treatment and during the reaction itself, have been refined[148]:

$$r_1 = k_1\omega e^{-\alpha c}P_1\gamma/(1 + k'P_1)^2, \quad (34)$$

$$r_3 = k_3P_1, \quad (35)$$

$$r_4 = k_4P_{C_4H_8}, \quad (36)$$

$$r_5 = k_5\omega P_{C_4H_8}/P_{H_2}. \quad (37)$$

Under the experimental conditions (535–585°C), the conversion of butenes into butadiene is reversible and the changes in ω are defined by equations for diffusion in a solid. A similar exponential dependence of the rate of the process on coke concentration characterises the kinetic models for the dehydrogenation of butane and isopentane in the presence of another alumina–chromium oxide catalyst[147,148]. A kinetic equation analogous to Eqn. (29) with $M = 1$, to which a linear decrease of the rate of reaction with increasing coke concentration corresponds, is valid for the dehydrogenation of isobutane to isobutene in the presence of an alumina–chromium oxide catalyst[146].

A study of the kinetics of the dehydrogenation of isopentenes to isoprene in the presence of a zinc–chromium [zinc oxide–chromium oxide?] catalyst[116-118,186] at 540 to

620°C using ^{14}C and deuterium led to the derivation of the equation

$$r = k^* \frac{P_1\gamma}{(P_1 + k'P_{C_5H_8})^{0.5}}, \quad (38)$$

where the constant k^* depends in the general case on the change in the free energy of the system ΔG_X for the given degree of conversion x, which affects the free energy of the catalyst surface (taken into account by the factor a), and also on the amount of coke:

$$k^* = k(1 - lc/c_{max})e^{-a\Delta G_x/RT} \quad (39)$$

(where l is a variable multiplier close to zero, reaching unity for $c = c_{max}$) and $a \simeq 1$. This equation corresponds to the scheme taking into account the slow abstraction of hydrogen from the most reactive isomer (2-methylbut-2-ene) accompanied by the attainment of isomerisation equilibrium. The changes in free energy have a marked influence on the rate of the process, causing considerable alterations in the latter for a small increase in the degree of conversion.

The same reaction in the presence of a nickel–phosphate catalyst is described by a more complex kinetic model[181–183] characterising the rate of dehydrogenation (r_1), the formation of light hydrocarbons from isopentenes (r_2), and coke formation (r_3) in the temperature range 580–680°C and also the rate of regeneration of the catalyst (r_6):

$$r_1 = k_1 \frac{P_1\gamma}{c^{2/3} + k'P_{C_5H_8}}, \quad (40)$$

$$r_2 = k_2 \frac{P_1}{c^{2/3} + k'P_{C_5H_8}}, \quad (41)$$

$$r_3 = \frac{k_3P_1 + k_3^*P_{C_5H_8}}{c^{2/3} + k'P_{C_5H_8}} + \frac{k_3'P_1 + k_3''P_{C_5H_8}}{(c^{2/3} + k'P_{C_5H_8})^{0.5}} c^{2/3} e^{-ac}, \quad (42)$$

$$r_6 = k_6 \frac{P_{O_2}c^{2/3}}{P_{O_2} + k_6'c^{2/3}}. \quad (43)$$

These equations follow from the general multistage mechanism (i.e. are not empirical), which presupposes that the reaction proceeds via reversible isomerisation stages, slow successive elimination of hydrogen from the adsorbed isopentenes, their cleavage, and coke formation on the free surface as well as the surface already occupied by coke. The experimental kinetic isotope effects obtained[183] agree with this mechanism.

The kinetics of cracking reactions under non-steady-state conditions, due to the decrease of the activity of the catalyst caused by the blocking of the active surface sites, have been considered by Wojciechowski (see his review[187]) on the basis of ideas which he developed. These refer only to the simplest instances of previously postulated mechanisms and lead to time-dependent non-autonomous models. The requirement that the model be independent of time is extremely important for its practical employment[140]. Models describing the decrease of activity have also been discussed in a number of other studies (see, for example, Refs. 188–192). Non-steady-state changes may arise as a consequence of the rearrangement of the active sites on the catalyst surface during the reaction and the formation of surface phases. The kinetics of such processes have been examined in a general form[193].

The formal kinetic descriptions of the reaction under steady- and non-steady-state conditions can naturally be significantly different. Certain simplest cases of such changes and transitions from one set of conditions to another have been discussed[170,194]. However, apart from the intrinsic non-steady state (see above), only the non-steady chemical state, in which the chemical composition of the catalyst is brought into correspondence with that of the gas phase after the attainment of adsorption equilibrium, has been examined in these investigations. This limitation rules out a general approach to this problem.

If the processes corresponding to the attainment of a steady state during the relaxation of the rate of reaction are considered for a fixed number of active sites on the catalyst surface, all the "extraneous" non-steady-state processes caused by the influence of some other factors (the influence of the reaction system, etc.) are as a rule associated with changes in the number or quality of active regions. The mechanism of such changes is in most cases insufficiently clear and a mathematical description taking them into account in kinetic models is much more complex than the description of the steady-state cases. A further development of experimental techniques and approaches to the interpretation and description of the results is therefore necessary for the investigation of the kinetics of non-steady-state processes. This is significant also owing to the practical importance of non-steady-state conditions, particular examples of which may arise in processes with a pseudofluodised catalyst bed or with a moving bed. The possibility of non-steady-state changes and the effectiveness of such, perhaps even brief non-steady-state conditions, which have proved to be more suitable than steady-state conditions[127,128], result in an extremely urgent need for studies designed to obtain and interpret non-steady-state kinetic models.

At the same time, since the bulk of catalytic industrial processes are nowadays carried out under steady-state conditions, further research on processes under steady-state conditions and establishment of steady-state kinetic models are equally necessary. Both types of research should naturally supplement one another, clearly under conditions where non-steady-state effects are real, currently important, and useful. The search for such non-steady-state effects can also prove extremely useful, which in no way diminishes the importance and the amount of information derivable from steady-state models which can lead to the process mechanism by a more direct and productive procedure.

The problems of non-steady-state kinetics may be the subject of a separate review.

V. OPTIMUM KINETIC MODELS

Each kinetic model must reflect real specific properties of the reaction–catalyst system investigated under the given conditions. If the kinetic equation for the reaction via one of the pathways is considered in a general form, it can be represented[48] as a product of the initial velocity r_0 ("reaction level") and a function of the degree of conversion $\Phi(x)$ (normalised to unity), which determines the form of the kinetic model:

$$r = r_0\Phi(x). \quad (44)$$

The level r_0 depends on the initial conditions, the amount of the catalyst, its activity and adsorption capacity, and the specific form of the kinetic equation, to which the function $\Phi(x)$ is extremely sensitive (see Fig. 7). Fig. 7 shows that changes in r relative to r_0, which are determined by the changes in $\Phi(x)$ during the process, from $x = 0$ to $x \simeq 1$, will be smallest for a zero-order reaction.

For other kinetic relations, there is a steady decrease of the reaction rate, which is more marked for higher-order reactions and when the reaction is strongly inhibited by its products. Relations with extrema are also possible, but these need not be discussed here, since they do not alter our conclusions.

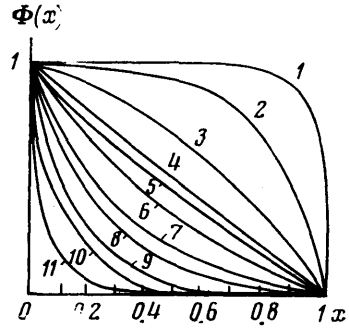


Figure 7. Dependence of the form of $\Phi(x)$ on the degree of conversion for different kinetic equations $r = kP_1^n/P_{prod}^m$: 1) $m = 0$, $n = 0$; 2) $n = 0.3$; 3) $n = 0.5$; 4) $n = 1$; 5) $n = 1.5$; 6) $n = 2$; 7) $n = 3$; 8) $m = n = 0.5$; 9) $m = 0.5$; $n = 2$; 10) $n = 0.5$, $m = 1$; 11) $n = m = 1$.

Thus the form of the kinetic model, specified by the kinetic equation, describes the nature of the changes in the rate of the process, throughout its course, under steady-state conditions. From this standpoint, one may speak of the optimum form of the kinetic model, reflecting the most convenient type of changes in the rate of the reaction throughout the latter. Since high or the maximum possible conversions (for the given selectivity) are of greatest interest for practical use, the minimum decrease of the rate of reaction compared with its initial value as the degree of conversion increases is the most convenient. The form of the kinetic model characterising the smallest changes in the reaction rate with increasing degree of conversion, other conditions being equal, may be regarded as the optimum form. It is clear from the foregoing that the form describing a zero-order reaction or other similar relations, in which the decrease of the rate of reaction during the process is a minimum compared with the relations corresponding to other kinetic equations possible for the given system, is the optimum form [149].

However, the fact that the model has the optimum form does not yet show that the model as a whole is optimum, which depends on the superposition of various factors. If we again restrict ourselves to a single stoichiometric reaction pathway, then, for the specified activity of the catalyst and the optimum form of the kinetic model, the latter is optimum as a whole when the level r_0 is higher than that corresponding to other kinetic models.

Thus the model which adequately describes the changes in the reaction rate during the process, which are the smallest possible compared with the initial level r_0 (r_0 being greater than other possible values obtained for other models under the specified conditions and for the specified catalyst activity), may be regarded as the optimum model. The optimum properties treated in this way depend on the internal characteristics of the process, which determine the given kinetic model. Consequently one may be dealing with kinetically optimum reaction mechanisms from which follow optimum kinetic models. The kinetically optimum reaction mechanism (which depends on the reaction conditions and the catalyst properties) will then be one ensuring that the optimum kinetic model arises from it, i.e. the most convenient form of the model and the most convenient initial process velocity. Hence it follows that, in selecting the catalyst, it is useful to take into account whether or not it can ensure a rate of the process whose value and the changes in the latter correspond to the optimum or nearly optimum kinetic model.

Analysis of the kinetic relations arising from various possible multistage process mechanisms and the relative rates of the stages may indicate which models are optimum or nearly optimum for the specified activation energy under the given conditions, together with approximate estimates of the rate constants for the elementary stages by the transition state method. Such analysis of the optimum properties of the models may constitute one of the stages in the selection of catalysts accompanied by the consideration of the possible properties and composition which would ensure the required kinetically optimum mechanism.

An estimate [149] has shown that the most convenient form of the model, i.e. the most nearly zero-order reaction, corresponds in most instances also to the highest level r_0 for the specified activation energy, provided that the reaction proceeds via slow stages involving surface interaction or desorption (the activation entropy is zero or higher). The initial velocities for different forms of the models proved to be extremely different and the replacement of a zero-order equation by other equations alters the level r_0 so much that the influence of the decrease in the latter on the rate of reaction may be compensated only by an improbably large decrease of activation energy.

Table 6. The degree of approach to an optimum by the kinetic models for certain reactions [149].

Reaction	Model characteristics	Remarks
Isomerisation of cyclohexene to methylcyclopentane on CaY zeolite (0.5% Pt); 268-320°C; 13-17 atm (Ref.150)	Zero-order equation corresponding to rapid formation of C_6H_{10ads} and its slow conversion into $C_5H_9CH_{3ads}$	Nearly optimum model
Hydrogenation of benzene on nickel; 90-150°C; 1 atm (Refs. 74,100)	The observed equation $r = kP_{H_2}^{0.5}$ is closer to a zero-order equation than other possible expressions; it corresponds to the slow conversion of C_6H_{6ads} into C_6H_{7ads} (Ref.151)	Model closer to an optimum under the given conditions than other models
Oxidation of hydrogen on oxide catalysts (Sn, Mo, W, Cd, Mn, V, Co, Cr, Cu, and Ni oxides) (Refs.152,153)	The rate of the process is described by a first-order equation with respect to hydrogen and corresponds to an oxidation-reduction mechanism or other multistage mechanisms.	Model closer to an optimum than the model corresponding to single-stage mechanisms.

Table 6 presents the results of the analysis [149] of certain simple models as regards their optimum properties, using literature data [74,100,150-153].

The kinetic models listed in Table 6 may be closer to the optimum model than others for the same reaction under different conditions or in the presence of other catalysts. For example [149], if the isomerisation of cyclohexene proceeded in a single stage (i.e. in accordance with

another model), its rate would be described by a first-order equation (and not a zero-order equation as in the model described above), with values of r smaller by several orders of magnitude (for the same experimental activation energy and under the same conditions). Consequently the model with the optimum form also corresponds to the highest initial velocity of the reaction.

It has been shown for the hydrogenation of benzene [48,74] that the rate of the process under the given conditions, characterised by the model in Table 6, is higher than when the process is described by other kinetic equations: $r = kP_1P_{H_2}$ or $r = kP_1^{0.5}P_{H_2}^3$.

Analysis [149] also leads to the conclusion that the rate of the reaction corresponding, for example, to the Parravano mechanism [195] (the slow stage involves the adsorption of hydrogen and its subsequent rapid interaction with benzene in the gas phase) would be described by a more complex kinetic relation and would be lower approximately by 8 orders of magnitude than for the model in Table 6. If Kagan's mechanism [96] were valid (slow formation of cyclohexadiene with subsequent rapid disproportionation), the kinetic equation for such a model would be complex with a sharper decrease of the rate of reaction compared with the initial value and the rates r under the specified conditions for the given activation energy would be in order of magnitude lower than for the model in Table 6 [149].

According to the results of Goncharuk and Golodets [152], the rate of oxidation of hydrogen in the presence of tungsten trioxide under conditions such that a first-order equation (which is closer to the optimum expression than the other observed kinetic relations) does not hold, proves to be an order of magnitude lower than in the presence of the same catalyst when the equation does hold. Comparison of the activation entropies for oxidation reactions carried out by Boreskov [154] also showed that the entropy is much higher for the oxidation-reduction mechanism than for a single-stage reaction. The form of the kinetic model is also much less favourable [149] for the single-stage mechanism. According to Popovskii et al. [153], the rate of oxidation of hydrogen in the presence of chromium trioxide at 226°C, where a kinetic equation with a fractional order holds ($r = k_0 e^{-20\,000/RT} P_{H_2}^{0.6}$), is approximately the same as in the presence of V_2O_5 at a much higher temperature (440°C), where a first-order kinetic equation $r = k_0 e^{-21\,000/RT} P_{H_2}$ is valid (evidently the activation energies are similar in the two cases and cannot be the cause of the discrepancy between the values of r at comparable temperatures). Consequently, for the form of the kinetic model closer to the optimum, which obtains in the presence of chromium oxide, the initial reaction rate is much higher than in the presence of V_2O_5, where the form of the model is further removed from the optimum.

The turnover number of the reaction [41] can serve as a quantitative characteristic of its initial level, because it refers, as a rule, to a degree of conversion of zero. Maatman [197] calculated the turnover numbers for different reactions and catalysts assuming in many instances that the reactions proceed in accordance with a zero-order equation and an activation entropy close to zero. If his values were sufficiently well-founded, the greatest turnover number would correspond precisely to the optimum model. Thus, according to his calculations [197], the turnover number for the cracking of cumene on a "decationated" zeolite is higher by many orders of magnitude than on an aluminosilicate catalyst. Thus Maatman's results show that, despite the optimum form of the kinetic models in the two instances, they differ sharply as regards the level of the reaction and therefore the first model must be regarded as optimum. Unfortunately, Maatman's calculations are not based on accurate kinetic data and accurate information about the reaction mechanism.

The above examples demonstrate the usefulness of the analysis of the optimum properties of kinetic models. In the selection of catalysts it is therefore useful to carry out an analysis in order to determine which kinetic models could describe the reaction in the presence of the selected catalyst and which additives (if the possible mechanism of their action is considered) could lead to other models closer to the optimum. Naturally such an approach is extremely simplified and one-sided, but, when the appropriate information is available, it can be very useful. Kol'tsov, Beskov, and the present author [196] considered in general terms the optimum process conditions which may be predicted from the form of kinetic models (references to preceding communications are given in this paper).

VI. KINETIC MODELS AND REACTION SELECTIVITIES

The selectivity is one of the most important kinetic factors characterising the course of complex reactions and determining their practical employment. It can be expressed as the ratio of the sum of the reaction rates via pathways leading to the formation of the desired product to the sum of the rates of all the transformation of the initial substances under identical conditions [156] ("differential selectivity" [155]). This ratio characterises the true process selectivity. Since the desired product can undergo secondary transformations, it is necessary to consider the apparent selectivity [156,157] taking into account the rate of accumulation of the desired product W_j as the algebraic sum of the rates of reaction via all the pathways leading to its formation and decomposition (for the given composition of the reaction mixture):

$$S = W_j/W_1, \qquad P_1^0, P_2^0, \ldots = \text{const}, \; x = \text{const}; \; T = \text{const}, \tag{45}$$

where W_1 is the overall rate of the transformations of the starting material. This expression for a reaction in a gradient-free system [1] is identical with the expression for the integral selectivity—the ratio of the amount of the desired product to the overall amount of all the products.

The changes in selectivity during the process evidently depend on its nature, which is determined by the properties of the kinetic model and the rates of reaction via different pathways. These changes, caused by the form of the dependence of the reaction rates on the degree of conversion which follows from the given kinetic model, may be different for different selectivities.

Such instances reflect a parallel process mechanism (where the desired product does not undergo further transformations on being separated from the catalyst), or a consecutive mechanism (the desired product is partly returned to the surface and is converted into side products), or a parallel-consecutive mechanism (a combination of the first two mechanisms). The expression for the selectivity covering these instances follows from Eqns. (44) and (45) [156,157,198]:

$$S = \left(1 - \eta \frac{\Phi_{III}(x_{III})}{\Phi_I(x_I)}\right) \Big/ \left(1 + \alpha \frac{\Phi_{II}(x_{II})}{\Phi_I(x_I)}\right). \tag{46}$$

Here subscripts I, II, and III indicate the pathways leading to the formation of the desired product and the parallel and consecutive formation of side products, $\alpha = r_0^{II}/r_0^{I} = \text{const}$.

(i.e. the initial reaction rates via parallel pathways do not vary during the process), but $\eta = r_0^{III}/r_0^{I} \neq$ const. (i.e. the initial rate of reaction via pathway III changes continuously owing to the changes in the concentration of the desired product); $\eta = 0$ for the parallel mechanism and $\alpha = 0$ for the consecutive mechanism.

Eqn. (46) indicates a direct relation between the form of the kinetic model and the changes in selectivity. From this it follows that the constancy of the selectivity during the process is possible only under certain conditions: (a) when the reaction proceeds in accordance with a zero-order equation via all the pathways (an unlikely case); (b) $\alpha \ll 1$ and $\eta \ll 1$ (i.e. reaction via the main pathway I predominates throughout the process) whereupon $S \simeq 1$; (c) when the process proceeds via a parallel mechanism, the kinetic equations for both pathways are identical, and there is no inhibition by the products.

Consequently the independence of the selectivity of the degree of conversion over a fairly wide range of the latter when S is appreciably different from unity may correspond only to a fully defined type of the kinetic model for the process. This is illustrated, for example, by the isotope exchange reaction in cyclohexane, discussed above, when its rates via all the parallel pathways are described by identical kinetic equations (Fig. 4). The properties of the kinetic model, characterised by identical kinetic equations in the absence of inhibition of the reaction via all the pathways by its products, determine the constancy of the ratios of the reaction rates via these pathways throughout the process. The latter is equivalent to the constancy of reaction selectivity for variable degrees of conversion [this should in its turn indicate the parallel formation of all the products, confirming the multistage mechanism (5)]. Evidently, the selectivity in the given instance serves as an additional factor whereby one can test and confirm the proposed kinetic model, which determines the observed characteristics of the selectivity (see also Butovskii et al.[182]).

An increase of selectivity during the processes is possible if the reaction via the required pathway is inhibited by its products to a lesser extent than via the remaining parallel pathways (for example, in the oxidation of cyclopentadiene [158]) or when the desired product is formed via several pathways and the formation of other products is inhibited by the initial substance. The latter case is observed in the oxidative ammonolysis of xylenes [159]. For example, isophthalonitrile is formed in this reaction from *m*-xylene in accordance with a second-order equation and the formation of extensive oxidation products is inhibited by the initial xylene, such products being obtained only from the initial xylene and the intermediate tolunitrile but not from the desired product (isophthalonitrile). One may therefore expect an increase of selectivity with increasing degree of conversion; this is in fact observed, which indicates the validity of the chosen kinetic model. Eqn.(46) shows that in other instances the selectivity should decrease during the process in conformity with numerous data [157].

Thus the properties of kinetic models determine to a significant extent the magnitude and nature of the changes in selectivity, which may be used in the analysis of kinetic relations.

Analysis of the changes in selectivity for processes described by different kinetic power equations is described in a book [199]. Golodets and coworkers [200-202] obtained and analysed expressions for the selectivity corresponding to the kinetic equations for certain oxidation reactions. The expressions can also be used in the analysis of kinetic models.

VII. ESTIMATION OF THE ACTIVITIES OF CATALYSTS OF COMPLEX REACTIONS

The problems associated with the tests, estimations, and comparison of the activities of catalysts are purely kinetic, since the only objective criterion of catalytic activity is the rate of reaction under the specified conditions and for the given composition of the reaction mixture [155,156,160,161]. For complex processes occurring via different pathways, the rate of accumulation of the desired product [156], i.e. the algebraic sum of the rates of reaction via independent pathways leading to its formation and decomposition, can serve as a criterion of the activity of catalysts. Since the rate of reaction depends on the degree of conversion, information about the rates of accumulation of the desired product for different compositions of the reaction mixture and for different conversions at the limits of the ranges of variation of the specified process parameters is desirable if sufficiently complete characteristics of the catalytic activity are to be obtained.

For objective tests and comparison of catalytic activities, exact measurements of the rate of reaction in the presence of distorting transport effects (and when internal-diffusion inhibition cannot be eliminated also with allowance for the latter) are necessary. It is useful to carry out such tests in gradient-free apparatus. The results of the tests can be expressed by "conversion curves" [48] relating the rate of reaction to the degree of conversion under specified initial process conditions.

The problem of tests of the activity of catalysts used under non-steady-state conditions is naturally more complicated. It requires the determination of the relation between the activity of the catalyst and various factors, particularly the duration of the continuous process, which depends in its turn on the concentration of impurities, the changes in the state of the catalyst as a consequence of the influence of the reaction system, etc. In this case it may be useful to combine tests in gradient-free apparatus with non-steady-state methods providing for the simultaneous monitoring of the state of the catalyst and the changes in the latter. Such methods are urgently required in preliminary studies and subsequent development [of the process?].

Exact tests and an objective estimate of catalytic activity and selectivity are evidently by no means easy and for complex reaction systems, for example for petroleum processing reactions, the problem is far from solution, although there are publications in this field [162,163]. However, despite the difficulties which must be faced in its solution (particularly in the case of tests of catalysts in non-steady-state processes), the magnitude of the problem is in no way comparable to the problem of devising kinetic models which requires a much greater expenditure of time and effort.

Despite this, further development of new effective and rapid methods for the testing of catalysts of complex reactions and the estimation of their activity and selectivity constitutes one of the most important problems of chemical kinetics in heterogeneous catalysis.

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In conclusion one may note that further development of the theory and practice of heterogeneous catalysis will depend to a considerable extent on the strength of its kinetic foundation. It is based on informative kinetic models for various catalytic processes. The valuable information which can be derived from these models should help in understanding the essential features of

catalytic activity and should extend the practical employment of catalysis. In order to set up such models, it is useful to carry out complex kinetic investigations. Although the methods for devising kinetic models and their analysis have been adequately developed, they require new approaches and further expansion, particularly for non-steady-state processes. The possibilities arising from complete, reliable, exact, and well-founded kinetic models, some of which were described above, make the task of their formulation and general treatment exceptionally important and necessary.

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